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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

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Mixed metal catalyst based on a combustible binder5 Field of the invention

The invention relates to catalysts comprising a Group VIII non-noble metal and a Group VIB metal on a combustible carrier, to the preparation of these catalysts, and to the use thereof in hydroprocessing applications. The invention further pertains to the recycling of used or waste catalysts comprising a Group VIII non-noble metal, a Group VIB metal, and a combustible binder.

Background of the invention

Conventional hydroprocessing catalysts generally contain a non-combustible binder. Used or waste catalysts are therefore rather difficult to recycle: e.g., when catalysts containing non-combustible binders together with Group VIB metals and Group VIII non-noble metals are recycled, the Group VIB metals are first leached, e.g., by contacting the catalyst with NaOH, resulting in a binder still containing the Group VIII non-noble metals. Subsequently, the Group VIII non-noble metals are separated from the binder by leaching with H₂SO₄. After that the various Group VIB metals and, if more than one is present, the various Group VIII non-noble metals must be separated from one another and further must be transformed into suitable salts. Such a recycling process is rather time consuming, nor can it be avoided in such a separation process that a portion of the expensive Group VIB and Group VIII metals remains on the binder and thus is lost.

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A newer trend is the development of bulk catalysts, i.e. catalysts not containing any binder at all. However, without a binder, the mechanical strength of the catalyst generally is rather low.

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It is therefore an object of the present invention to provide catalysts which are highly active in hydroprocessing, which have a high mechanical strength, and which can easily be recycled after use.

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Summary of the invention

It has now surprisingly been found that the above objectives can be met by employing a combustible binder or a precursor thereof in the catalyst preparation process. This combustible binder not only gives the catalyst sufficient mechanical strength but also can easily be removed from the used catalyst by a thermal treatment. A sophisticated separation of the binder from the Group VIB and Group VIII metals thus is not required anymore.

In a preferred embodiment of the present invention, the catalyst is prepared using at least one Group VIII non-noble metal and at least two Group VIB metals. This leads to catalysts with an improved performance in hydroprocessing applications which are easily recyclable and which have, at the same time, a high mechanical strength.

Catalysts containing at least one Group VIII non-noble metal and at least two Group VIB metals and processes for the preparation thereof are known from, e.g., JP 09000929, US 4,596,785, US 4,820,677, US 3,678,124, US 4,153,578, WO 9903578, and non-prepublished international patent applications PCT/EP00/00354 and PCT/EP00/00355.

The catalyst of JP 09000929 is prepared by impregnating an inorganic non-combustible support with cobalt or nickel as the Group VIII non-noble metal and molybdenum and tungsten as the Group VIB metals.

The catalyst of US 4,596,785 comprises the disulphides of at least one Group VIII non-noble metal and at least one Group VIB metal. The catalyst of US 4,820,677 comprises an amorphous sulphide comprising iron as the Group VIII non-noble metal and a metal selected from molybdenum, tungsten or mixtures thereof as the Group VIB metal, as well as a polydentate ligand such as ethylene diamine. In both references the catalyst is prepared via the co-precipitation of water-soluble sources of one Group VIII non-noble metal and two Group VIB metals in the presence of sulphides. The precipitate is isolated, dried, and calcined in an inert

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atmosphere. The catalysts of these references are either binder-free or may contain an inorganic non-combustible binder, such as alumina.

5 US 3,678,124 discloses oxidic catalysts to be used in the oxidative dehydrogenation of paraffin hydrocarbons. The catalysts are prepared by co-precipitating water-soluble components of the Group VIB metals and Group VIII non-noble metals. The catalysts are either binder-free or contain an inorganic, non-combustible binder.

10 The catalyst of US 4,153,578 is a Raney nickel catalyst which is prepared by contacting Raney nickel optionally containing, e.g., tungsten with a molybdenum component in the presence of water. Molybdenum is adsorbed on the Raney nickel by stirring the resulting suspension at room temperature.

15 In WO 9903578, catalysts are prepared by co-precipitating certain amounts of a nickel, molybdenum, and tungsten source in the absence of sulphides. The catalyst is either binder-free or may contain an inorganic non-combustible binder.

20 Non-prepublished international patent application PCT/EP00/00354 discloses the preparation of sulphided catalyst compositions by coprecipitation of at least one Group VIII non-noble metal component and at least two Group VIB metal components to form an oxygen-stable precipitate, which is subsequently sulphided. Non-prepublished international patent application PCT/EP00/00355 discloses the preparation of a catalyst composition by contacting at least one
25 Group VIII non-noble metal component and at least two Group VIB metal components in the presence of a protic liquid, wherein at least one of the metal components is at least partly in the solid state during contacting. The catalysts of non-prepublished international patent applications PCT/EP00/00354 and
30 PCT/EP00/00355 are either binder-free or may contain an inorganic incombustible binder.

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Consequently, the catalysts of the above references either are binder-free or comprise a non-combustible binder. A catalyst comprising a combustible binder is neither disclosed nor suggested in these references.

5 Detailed description of the invention

Catalyst preparation process

The present invention pertains to a process for preparing a catalyst composition comprising a Group VIII non-noble metal, a Group VIB metal, and a combustible binder, wherein the catalyst comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition, which process comprises contacting a Group VIII non-noble metal component with a Group VIB metal component in the presence of a liquid, wherein a combustible binder material selected from a combustible binder or a precursor thereof is added prior to, during and/or subsequent to the contacting of the metal components, with the proviso that at least if the combustible binder material consists essentially of a precursor of a combustible binder, this precursor is converted into a combustible binder subsequent to its addition.

In a preferred embodiment of the present invention, the catalyst comprises at least one Group VIII non-noble metal and at least two Group VIB metals. Consequently, a preferred embodiment of the present invention pertains to a process for preparing a catalyst composition comprising at least one Group VIII non-noble metal, at least two Group VIB metals, and a combustible binder, wherein the catalyst comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition, which process comprises contacting at least one Group VIII non-noble metal component with at least two Group VIB metal components in the presence of a liquid, wherein a combustible binder material selected from a combustible binder or a precursor thereof is added prior to, during and/or subsequent to the contacting of the metal components, with the proviso that at least if the combustible binder material consists essentially of a precursor of a combustible binder, this precursor is converted into a combustible binder subsequent to its addition.

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Generally, there are two possible ways of contacting the metal components with one another, namely by combining and reacting the metal components in solution to form a precipitate (hereinafter designated as the "solution route"), or by combining⁵ and reacting the metal components in the presence of a protic liquid with at least one of the metal components remaining at least partly in the solid state (hereinafter designated as the "solid route").

In the solution route, the metal components are completely dissolved when they are combined and/or reacted to form a precipitate. It is possible, e.g., to combine
10 the metal components when they are already in the dissolved state and then have them react to form a precipitate. However, it is also possible to combine one or more of the metal components which are partly or entirely in the solid state with further metal components. However, in this case, care must be taken that the metal components which are partly or entirely in the solid state will dissolve when
15 present in the reaction mixture. In other words, at least once during the solution route process, all metal components must be present wholly as a solution. In cases where metal components are combined partly or entirely in the solid state, the metals are actively dissolved in the reaction mixture, for instance by stirring, increasing the amount of solvent, changing the solvent, changing the temperature,
20 or changing the pH or adding a complexing agent which leads to the formation of a soluble complex of the metal.

Precipitation can be effected by, e.g.,

- 25 (a) changing the pH during or after combination of the metal component solutions to such a value that precipitation is induced;
- (b) adding a complexing agent during or after combination of the metal component solutions, which complexing agent complexes one or more of the metals to prevent precipitation of the metals, and thereafter changing the reaction conditions, such as temperature or pH, such that the complexing
30 agent releases the metals for precipitation;
- (c) adjusting the temperature during or after combination of the metal component solutions to such a value that precipitation is induced;

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- (d) lowering the amount of solvent during or after combination of the metal component solutions such that precipitation is induced;
- (e) adding a non-solvent during or after combination of the metal component solutions to induce precipitation thereof, with a non-solvent meaning that the precipitate is essentially insoluble in this solvent;
- (f) adding an excess of either of the components to such an extent that precipitation is induced.

Adjusting the pH in, e.g., option (a) or (b) can be done by adding a base or an acid to the reaction mixture. However, it is also possible to add compounds which upon the temperature increasing will decompose into hydroxide ions or H^+ ions, which increase and decrease the pH, respectively. Examples of compounds which will decompose upon the temperature increasing and thereby increase or decrease the pH are urea, nitrites, ammonium cyanate, ammonium hydroxide, and ammonium carbonate.

As will be clear from the above, it is possible to add the Group VIII non-noble metal component and the Group VIB metal component in various ways: at various temperatures and pHs, in solution, in suspension, wetted and as such, simultaneously and sequentially. Of course, if they are added as a suspension, wetted or as such, they must dissolve in the reaction mixture. Preferably, the metal components are added in the form of their solutions.

Suitable solvents, Group VIII non-noble metal components, Group VIB metal components, as well as further details and preferred embodiments are given in non-published international patent application PCT/EP00/00354 under the heading "Catalyst preparation process" under "Process step (i)." This paragraph is incorporated into the present specification by way of reference. It should be noted that it is preferred that not to employ sulphur-containing metal components, as these components and the resulting products are not stable in relation to oxygen, which implies that all process steps subsequent to the addition of this metal component, even those at a lower temperature, will have to be applied under an inert atmosphere.

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The solid route comprises combining and reacting the metal components, with at least one of the metal components remaining at least partly in the solid state. More in particular, it comprises adding the metal components to one another and simultaneously and/or thereafter reacting them. Consequently, in the solid route at least one metal component is added at least partly in the solid state and this metal component remains at least partly in the solid state during the entire reaction. The term "at least partly in the solid state" in this context means that at least part of the metal component is present as a solid metal component and, optionally, another part of the metal component is present as a solution in the protic liquid. A typical example of this is a suspension of a metal component in a protic liquid, where the metal is at least partly present as a solid, and optionally partly dissolved in the protic liquid.

It is possible to first prepare a suspension of a metal component in the protic liquid and to add, simultaneously or successively, solution(s) and/or further suspension(s) comprising metal component(s) dissolved and/or suspended in the protic liquid. It is also possible to first combine solutions either simultaneously or successively and to subsequently add further suspension(s) and optionally solution(s) either simultaneously or successively.

As long as at least one metal component is at least partly in the solid state during the solid route, the number of metal components which are at least partly in the solid state is not critical. Thus it is possible for all metal components to be combined in the solid route to be applied at least partly in the solid state. Alternatively, a metal component which is at least partly in solid state can be combined with a metal component which is in the solute state. E.g., one of the metal components is added at least partly in the solid state and, e.g., at least two and preferably two metal components are added in the solute state. In another embodiment, e.g., two metal components are added at least partly in the solid state and at least one and preferably one metal component is added in the solute state.

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That a metal component is added "in the solute state" means that the whole amount of this metal component is added as a solution in the protic liquid.

5 Suitable protic liquids, Group VIII non-noble metal components, Group VIB metal components, as well as further details and preferred embodiments, e.g., in respect of the properties of the metal component which remains at least partly in the solid state, the retention of the morphology, or the process conditions during the combination and reaction of the metal components are given in non-prepublished international patent application PCT/EP00/00355 under the heading "Process of
10 the invention" under "(A) Preparation of bulk catalyst particles," which section is incorporated into the present specification by way of reference. As in the case of the solution route, it is preferred that no sulphur-containing metal components are employed. It is further preferred to use Group VIII non-noble metal salts as the Group VIII non-noble metal components.

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As stated above, preferably at least one Group VIII non-noble metal component and at least two Group VIB metal components are employed in the process of the invention. Suitable Group VIB metals include chromium, molybdenum, tungsten, or mixtures thereof, with a combination of molybdenum and tungsten being most
20 preferred. Suitable Group VIII non-noble metals include iron, cobalt, nickel, or mixtures thereof, preferably cobalt and/or nickel. Preferably, a combination of metal components comprising nickel, molybdenum, and tungsten or nickel, cobalt, molybdenum, and tungsten, or cobalt, molybdenum, and tungsten is employed in the process of the invention.

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It is preferred that nickel and/or cobalt make up at least 50 wt% of the total of Group VIII non-noble metals, more preferably at least 70 wt%, still more preferably at least 90 wt%. It may be especially preferred for the Group VIII non-noble metal to consist essentially of nickel and/or cobalt.

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It is preferred that molybdenum and tungsten make up at least 50 wt% of the total of Group VIB metals, more preferably at least 70 wt%, still more preferably at least

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90 wt%. It may be especially preferred for the Group VIB metal to consist essentially of molybdenum and tungsten.

5 The molar ratio of Group VIB metals to Group VIII non-noble metals employed in the process of the invention generally ranges from 10:1 - 1:10 and preferably from 3:1 - 1:3. The molar ratio of the different Group VIB metals one to the other generally is not critical. The same holds when more than one Group VIII non-noble metal is employed. When molybdenum and tungsten are employed as Group VIB metals, the molybdenum:tungsten molar ratio preferably lies in the range of 9:1 - 10 1:19, more preferably 3:1 - 1:9, most preferably 3:1 - 1:6.

As stated above, the catalyst composition of the present invention is prepared in such a way that it comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition. The amount of 15 carbon is determined as described below under "Characterization methods."

As further stated above, the combustible binder material is added prior to, during and/or subsequent to the contacting of the metal components. If the combustible binder material is added prior to and/or during the contacting of the metal 20 components, it preferably does not interfere with the reaction of the metal components. Generally, the addition of the combustible binder material subsequent to the contacting of the metal components is preferred.

25 The combustible binder material can be added prior to the contacting of the metal components by, e.g., adding it to one or more but not all of the metal components or vice versa, and by subsequently adding the not yet added metal components either simultaneously or successively.

30 The combustible binder material can be added during the contacting of the metal components by, e.g., simultaneously combining the combustible binder material and the metal components or first combining the metal components either simultaneously or successively and then adding the combustible binder material during the reaction of the combined metal components.

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The combustible binder material can be added subsequent to the contacting of the metal components by, e.g., adding it directly to the reaction mixture obtained after the reaction of the metal components. However, it is also possible to add the combustible binder material after a solid-liquid separation, a washing step or any of the further process steps which will be discussed in detail below.

Optional further process steps are, e.g., spray-drying, (flash) drying, milling, kneading, slurry-mixing, dry or wet mixing, shaping, calcining and/or sulphiding.

10 Dry mixing means mixing the catalyst composition in the dry state with, e.g., the combustible binder material in the dry state. Wet mixing, e.g., comprises mixing the wet filter cake comprising the catalyst composition and, optionally, e.g., the combustible binder material as liquid, powder or wet filter cake to form a homogenous paste thereof. Shaping comprises, e.g., extrusion, pelletizing,

15 beading and/or spray-drying. Calcination, if any, is generally performed at a temperature of, e.g., from 100° - 600°C, preferably from 150° to 550°C, more preferably 150°C - 450°C, for a time varying from 0.5 to 48 hours. The calcination can be carried out, e.g., in an oxygen-containing atmosphere, such as air. If the calcination is carried out in an oxygen-containing atmosphere, a calcination

20 subsequent to the addition of the combustible binder material generally should be avoided, as such a calcination would remove the combustible binder from the catalyst composition and thus reduce its mechanical strength. Sulphidation can, e.g., be carried out as described, e.g., in non-prepublished international patent application PCT/EP00/00354 (heading "Catalyst preparation process" under

25 "Process step (ii)," which section is incorporated into the present specification by way of reference). For further details in respect of these further process steps, reference is made to non-prepublished international patent applications PCT/EP00/00354 (heading "Catalyst preparation process" under "Process step (ii)" and "Further optional process steps") and PCT/EP00/00355 (heading

30 "Process of the invention" under "(B) Subsequent process steps"), which sections are incorporated into the present specification by way of reference.

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"A combustible binder material" in the sense of the present invention means one or more combustible binder(s) or precursor(s) thereof. If the combustible binder material comprises more than one combustible binder or precursor thereof, each binder or binder precursor can be added at any stage prior to, during or subsequent to the contacting of the metal components. One binder or binder precursor may, e.g., be added prior to the contacting of the metal components and another binder or binder precursor may be added subsequent to the contacting of the metal components.

10 A combustible binder in the sense of the present invention means any binder which is inert under hydroprocessing conditions and which is converted to gaseous compounds, such as carbon dioxide, in air at a temperature above 230°C. Inert "under hydroprocessing conditions" in the sense of the present invention means that the combustible binder is inert in a hydrogen atmosphere up to a temperature of at least 200°C. "Inert" in the sense of the present invention means that the combustible binder does not decompose, as can easily be verified by way of, e.g., TGA analysis.

The combustible binder preferably comprises carbon as its major component and optionally further comprises, e.g., O, H, and/or N. Typical examples are carbon powder, graphite, activated carbon, pyrocarbon, pyrographite, carbon black, all in combination with, e.g., the organic polymers given as combustible binder precursors below, such as polyfurfuryl alcohol. Further examples of combustible binders are, e.g., soot and at least partly carbonized organic polymers, such as the organic polymers given as combustible binder precursors below. It is noted that generally at least partial carbonization is necessary to render the polymer inert under hydroprocessing conditions. If however, a polymer is employed which in itself is inert under hydroprocessing conditions, such a carbonization step may be omitted.

If so desired, two or more combustible binders can be employed, optionally in combination with one or more combustible binder precursors.

A combustible binder precursor preferably is selected from the group of organic polymers, such as polyacrylonitriles, bakelite, polyamides, such as nylon,

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polyurethanes, cellulose and derivatives thereof, hemicellulosic materials, polyfurfuryl alcohol, styrene-divinylbenzene copolymers, phenol resins, furan resins, polyimide resins, polyphenylene resins, phenolic foams, and polyurethane foams. If so desired, two or more combustible binder precursors can be employed, optionally in combination with one or more combustible binders.

At least if the combustible binder material consists essentially of a combustible binder precursor, the process comprises a step in which the combustible binder precursor is converted into the corresponding combustible binder. Such a process step may be, e.g., pyrolysis in an inert atmosphere leading to the at least partial carbonization of the binder precursor. Preferably, the inert atmosphere comprises an inert gas, such as nitrogen. Most preferably, the inert atmosphere is essentially free of oxygen. Such pyrolysis preferably is carried out at a temperature of 300° - 600°C and more preferably 350° - 600°C. In principle, also higher temperatures may be applied for the conversion of the combustible binder precursor into the combustible binder. However, in order not to harm the further catalyst constituents, higher temperatures are less preferred. Alternatively, the conversion of the combustible binder precursor into the combustible binder may be carried out by a thermal treatment in an oxygen-containing atmosphere at a temperature below 230°C. If such a treatment in an oxygen-containing atmosphere is carried out subsequent to pyrolysis in an inert atmosphere, higher temperatures up to 350°C or even up to 500°C may be applied as thermal treatment. This is due to the fact that the ignition temperature of the combustible binder precursor generally is increased by the pyrolysis, so that in the subsequent thermal treatment in the oxygen-containing atmosphere higher temperatures can be applied without igniting the combustible binder precursor.

A further alternative is a high-temperature steaming treatment in the absence of oxygen.

However, generally, a thermal treatment in an oxygen-containing atmosphere may lead to the at least partial oxidation or even the combustion of the combustible binder precursor. Therefore, preferably, the conversion of the combustible binder precursor into the combustible binder is carried out by pyrolysis, as described above. As will be known to the skilled person, the temperature ranges for the

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pyrolysis as well as for the thermal treatment, if any, will depend on the type of combustible binder precursor employed and can easily be determined by, e.g., TGA analysis

- 5 The conversion of the combustible binder precursor into the combustible binder can be carried out at any stage of the process of the invention subsequent to the addition of the combustible binder precursor. If a mixture of a combustible binder and a combustible binder precursor is employed, such a process step, though no longer essential, is still preferred.

10

If so desired, the combustible binder or combustible binder precursor may be subjected to a reaction with, e.g., phosphorus- or nitrogen-containing compounds in order to introduce functional groups into the combustible binder (precursor).

- 15 The combustible binder material can be added, e.g., as a liquid or powder. In this case, the combustible binder material preferably is added prior to a shaping step. This process embodiment may, e.g., comprise the successive steps of contacting the metal components via either the solid or the solution route, isolating the catalyst composition via filtration, wet mixing the filter cake with the combustible
20 binder material, kneading, extruding, drying, and sulphiding the resulting composition. Another example comprises the successive steps of adding the combustible binder material prior to or during the contacting of the metal components according to the solid or the solution route, isolating the catalyst composition via filtration, kneading, extruding, drying, and sulphiding the resulting
25 composition. If the combustible binder material is a combustible binder precursor, the process embodiments must further comprise, e.g., a pyrolysis to convert the combustible binder precursor into the combustible binder.

- 30 Alternatively, a shaped combustible binder material can be employed, such as a shaped carbon carrier. In this case, the metal components preferably are contacted in the presence of the shaped combustible binder material. If the metal components are contacted according to the solution route, the Group VIB metals and Group VIII non-noble metals will predominantly be located in the pores of the

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- shaped combustible binder material in the final catalyst composition. Such a shaped combustible binder material preferably has a pore volume of at least 0.5 ml/g, more preferably of at least 1 ml/g, as measured by nitrogen adsorption. A shaped combustible binder material can also be employed in the solid route. In this case, e.g., the metal component which remains at least partly in the solid state may be co-shaped, e.g., co-extruded with the combustible binder material, and the resulting shaped material can be contacted with the metal components which are employed in the solute state.
- 5
- 10 To obtain catalysts with sufficient mechanical strength, it is essential that the amount of combustible binder material is such that the final catalyst composition contains at least 1 wt% of carbon, based on the total weight of the catalyst composition. Preferably, the amount of combustible binder material is such that the final catalyst composition will comprise carbon in an amount in the range of 1 -
- 15 75 wt% of the total composition, preferably 1 - 50 wt%, more preferably 2 - 30 wt%, and most preferably 4 - 30 wt%.

- Additionally, further materials such as phosphorus-containing compounds, boron-containing compounds, silicon-containing compounds, fluorine-containing
- 20 compounds, additional transition metal compounds, rare earth metal compounds, or mixtures thereof can be added during the contacting of the metal components and/or subsequent thereto. For details, reference is again made to non-prepublished international patent application PCT/EP00/00355 (heading "Process of the Invention" under "(A) Preparation of bulk catalyst particles" and "(B)
- 25 Subsequent process steps").

- Preferably, less than 10 wt%, more preferably less than 7 wt%, still more preferably less than 4 wt% and most preferably essentially no non-combustible binder selected from the group of silica, silica-alumina, such as conventional silica-
- 30 alumina, silica-coated alumina, and alumina-coated silica, alumina such as (pseudo)boehmite, or gibbsite, titania, titania-coated alumina, zirconia, cationic clays or anionic clays such as saponit, bentonite, kaolin, sepiolite or hydrotalcite, or mixtures thereof is employed in the process of the present invention.

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The process of the present invention can be carried out both as a batch process and as a continuous process.

5 Catalyst composition of the invention

The invention further pertains to a catalyst composition obtainable by the above-described process.

10 Furthermore, the invention pertains to a catalyst composition comprising a Group VIII non-noble metal, a Group VIB metal, and a combustible binder, wherein the catalyst comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition.

15 Preferably, the catalyst composition comprises at least one Group VIII non-noble metal and at least two Group VIB metals.

20 It is further preferred that the catalyst composition comprises 1 - 75 wt%, more preferably 1 - 50 wt%, even more preferably 2 - 30 wt%, and most preferably 4 - 30 wt% of carbon, based on the total weight of the catalyst composition. The amount of carbon is determined as described below under "Characterization methods."

25 The combustible binder preferably comprises carbon as its major component, optionally in combination with, e.g., O, H and/or N. For details, reference is made to the chapter "Catalyst preparation process" of this application.

30 If the catalyst has been prepared according to the solid route and is in its oxidic state (i.e., prior to any sulphidation treatment having been applied), it preferably has an X-ray diffraction pattern and in particular a characteristic full width at half maximum as described in non-prepublished international patent application PCT/EP00/00355 (heading "Catalyst composition of the invention" under "oxidic catalyst composition," which specification is incorporated into the present specification by way of reference).

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If so desired, the catalyst composition may comprise any further materials such as phosphorus-containing compounds, boron-containing compounds, silicon-containing compounds, fluorine-containing compounds, additional transition
5 metals, rare earth metals, or mixtures thereof.

The Group VIB metals and Group VIII non-noble metals are preferably chosen from the metals given above for the preparation of the catalyst composition. The molar ratio of Group VIB metals to Group VIII non-noble metals generally ranges
10 from 10:1 - 1:10 and preferably from 3:1 - 1:3. If more than one Group VIII non-noble metal or more than one Group VIB metal is employed, neither the ratio of the Group VIII non-noble metals one to the other nor the ratio of the Group VIB metals one to the other is critical. In cases where molybdenum and tungsten are present as Group VIB metals, the molybdenum:tungsten ratio preferably lies in the
15 range of 9:1 - 1:19, more preferably 3:1 - 1:9, most preferably 3:1 - 1:6.

It is preferred that nickel and/or cobalt make up at least 50 wt% of the total of Group VIII non-noble metals, more preferably at least 70 wt%, still more preferably at least 90 wt%. It may be especially preferred for the Group VIII non-noble metal
20 to consist essentially of nickel and/or cobalt.

It is preferred that molybdenum and tungsten make up at least 50 wt% of the total of Group VIB metals, more preferably at least 70 wt%, still more preferably at least 90 wt%. It may be especially preferred for the Group VIB metal to consist
25 essentially of molybdenum and tungsten.

The catalyst composition will preferably comprise 25 - 99 wt%, more preferably 50 - 99 wt%, still more preferably 70 - 95 wt% of the Group VIB metals and Group VIII non-noble metals, calculated as oxides and based on the total weight of the
30 catalyst composition. The amount of Group VIB metals and Group VIII non-noble metals can be determined via AAS or ICP.

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Preferably, the catalyst composition comprises less than 10 wt%, more preferably less than 7 wt%, still more preferably less than 4 wt%, and even more preferably essentially no non-combustible binders selected from the group of silica, silica-alumina, such as conventional silica-alumina, silica-coated alumina, and alumina-coated silica, alumina such as (pseudo)boehmite, or gibbsite, titania, titania-coated alumina, zirconia, cationic clays or anionic clays such as saponite, bentonite, kaolin, sepiolite or hydrotalcite, or mixtures thereof. That the catalyst composition essentially contains no non-combustible binder means that no such non-combustible binder has been added during the preparation of the catalyst. It does not exclude that such non-combustible binders are present in small amounts as a contamination of the catalyst.

Preferably, the catalyst compositions in their oxidic state, i.e., prior to any sulphidation step, have a B.E.T. surface area of at least 10 m²/g, more preferably of at least 50 m²/g, and most preferably of at least 80 m²/g, as measured via the B.E.T. method.

Preferably, the Group VIB metals and Group VIII non-noble metals are homogeneously distributed within the combustible binder. As stated above, the presence of the combustible binder leads to an increased mechanical strength of the final catalyst composition. Generally, the catalyst composition of the invention has a mechanical strength, expressed as side crushing strength, of at least 1 lbs/mm and preferably of at least 3 lbs/mm (measured on extrudates with a diameter of 1 - 2 mm).

The median pore diameter (50% of the pore volume is below said diameter, the other 50% above it) of the oxidic catalyst composition preferably is 3 - 25 nm, more preferably 5 - 15 nm (determined by N₂ adsorption).

The total pore volume of the oxidic catalyst composition preferably is at least 0.05 ml/g and more preferably at least 0.1 ml/g, as determined by N₂ adsorption.

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It is desired that the pore size distribution of the oxidic catalyst composition is of the same order as that of conventional hydroprocessing catalysts. More in particular, the catalyst composition preferably has a median pore diameter of 3 - 25 nm, as determined by nitrogen adsorption, a pore volume of 0.05 - 5 ml/g, more preferably of 0.1 - 4 ml/g, still more preferably of 0.1 - 3 ml/g, and most preferably of 0.1 - 2 ml/g, as determined by nitrogen adsorption.

Prior to any shaping step, the catalyst composition generally comprises particles having a median particle size in the range of at least 0.5 μm , preferably of at least 1 μm , most preferably of at least 2 μm , but preferably of not more than 5,000 μm , more preferably of not more than 1,000 μm , even more preferably of not more than 500 μm , and most preferably of not more than 150 μm . More preferably still, the median particle diameter lies in the range of 1 - 150 μm and most preferably in the range of 2 - 150 μm .

To further increase the mechanical strength, it may be desirable for the oxidic catalyst composition of the invention to have a low macroporosity. Preferably, less than 30% of the pore volume of the catalyst composition is in pores with a diameter larger than 100 nm (determined by mercury intrusion, contact angle: 130°), more preferably less than 20% is.

If a shaping step is applied, the resulting shaped catalyst composition may have many different shapes. Suitable shapes include spheres, cylinders, rings, and symmetric or asymmetric polylobes, for instance tri- and quadrulobes. Particles resulting from extrusion, beading or pelleting usually have a diameter in the range of 0.2 to 10 mm, and their length likewise is in the range of 0.5 to 20 mm. Particles resulting from spray-drying generally have a median particle diameter in the range of 1 μm - 100 μm .

30 Use according to the invention

The catalyst composition according to the invention can be used in virtually all hydroprocessing processes to treat a plurality of feeds under wide-ranging reaction conditions, e.g., at temperatures in the range of 200 to 450°C, hydrogen

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pressures in the range of 5 to 300 bar, and space velocities (LHSV) in the range of 0.05 to 10 h⁻¹. The term "hydroprocessing" in this context encompasses all processes in which a hydrocarbon feed is reacted with hydrogen at elevated temperature and elevated pressure, including hydrogenation, hydrodesulphurization, hydrodenitrogenation, hydrodemetallization, hydrodearomatization, hydroisomerization, hydrodewaxing, hydrocracking, and hydrocracking under mild pressure conditions, which is commonly referred to as mild hydrocracking. The catalyst composition of the invention is particularly suitable for hydrotreating hydrocarbon feedstocks. Such hydrotreating processes comprise, e.g., hydrodesulphurization, hydrodenitrogenation, and hydrodearomatization of hydrocarbon feedstocks. Suitable feedstocks are, e.g., middle distillates, kero, naphtha, vacuum gas oils, and heavy gas oils. Conventional process conditions can be applied, such as temperatures in the range of 250°-450°C, pressures in the range of 5-250 bar, space velocities in the range of 0,1-10 h⁻¹, and H₂/oil ratios in the range of 50-2000 NI/l.

Recycling process of the invention

As stated above, the binder of the catalyst composition of the present invention can easily be removed from the catalyst composition by a thermal treatment. Consequently, the present invention also pertains to a process for recycling a used or waste catalyst composition comprising a Group VIII non-noble metal, a Group VIB metal, and a combustible binder, wherein the catalyst comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition, which process comprises thermally treating the used or waste catalyst composition in an oxygen-containing atmosphere at a temperature of at least 300°C. Preferably, the thermal treatment is carried out in air. Preferably, the temperature is chosen above 400°C, more preferably above 500°C, even more preferably above 600°C, and most preferably above 700°C, but preferably below 850°C. The resulting Group VIB metal components and Group VIII non-noble metal components may be recovered in any conventional way, such as is described in *Catalysis Today*, 30 (1996) 223 (review of E. Furimsky, *Spent refinery catalysts: environment, safety and utilization*, chapter 4.1.1). It is noted that irrespective of the method chosen, the recovery process is simplified significantly

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by the absence of a binder. Depending on the recovery method applied, the resulting Group VIB metal components and Group VIII non-noble metal components may all be in the form of solutions, in which case they can be applied directly in the solution route, or else in the solid route after precipitation of at least one metal component. If at least one of the recovered metal components is in the form of a solid, the metal components can be applied directly in the solid route, or else in the solution route after dissolution of the solid metal component(s).

For preferred embodiments of the used or waste catalysts, e.g., in respect of the Group VIB metals and Group VIII non-noble metals or the amount of carbon, reference is made to the preferred embodiments of the catalyst of the present invention.

Characterization methods

15 (a) Side crushing strength (SCS)

The side crushing strength was determined as described in non-prepublished International patent applications PCT/EP00/00354 and PCT/EP00/00355.

(b) Pore volume

20 The pore volume was determined as described in non-prepublished international patent applications PCT/EP00/00354 and PCT/EP00/00355.

(c) Stability of the combustible binder via thermogravimetric analysis (TGA)

25 Samples were heated in a preselected atmosphere at a heating rate of 10°C/minute and the mass change of the sample was recorded over time. The preselected atmosphere chosen was the gas composition, in which the stability of the combustible binder is to be tested. Further details about TGA can be found in *Appl. Chem.*, 52 (1980) No. 1, 2385-2391.

30 (d) Carbon content

To determine its carbon content, the catalyst composition was subjected to heating in an induction oven under an oxygen flow. Any carbon contained in the catalyst composition was thus oxidized to carbon dioxide. The carbon dioxide was

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analyzed using an infrared cell with a detection system based on its IR characteristics. The resulting signals were compared with the signals of calibrated standards to obtain the amount of carbon dioxide and thus the amount of carbon contained in the catalyst composition.

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The present invention is further illustrated by the following examples:

Example 1

(a) Preparation of a catalyst composition of the invention:

10 A mixed metal composition was prepared by the solid route from nickel hydroxycarbonate, MoO_3 , and H_2WO_4 . The resulting precipitate was filtered and a wet filter cake was obtained containing about 20 wt% MoO_3 , 40 wt% WO_3 , and 40 wt% NiO (determined after calcination at 300°C in air).

15 A combustible binder precursor was prepared from furfuryl alcohol by mixing 200 ml of furfuryl alcohol with 200 ml of water and 1 ml of concentrated sulphuric acid, slowly heating the resulting mixture to 90°C , and keeping it at 90°C for 10 minutes. A two-phase system was obtained. The organic phase (containing the polyfurfuryl alcohol) was separated from the aqueous phase in a separation funnel, resulting in 55.6 g of organic liquid

20 500 g of the wet filter cake of the mixed metal composition on a dry base was mixed with the organic liquid. The water content of the mixture was adjusted by heating, so that an extrudable mix was obtained. The mixture was then extruded and dried at 120°C in air for 2 hours.

25 To convert the combustible binder precursor into a combustible binder, the resulting composition was heated at 300°C in flowing nitrogen for 2 hours.

(b) Characterization of the resulting catalyst composition:

30 The catalyst composition had a side crushing strength (SCS) of $5.6 \text{ lbs} \cdot \text{mm}^{-1}$. The carbon content was 4.83 wt%. It could be confirmed by TGA that the catalyst composition is stable under hydrogen atmosphere (50 vol% hydrogen in helium) up to a temperature of 270°C . It could further be confirmed by TGA that the combustible binder can be removed from the catalyst composition by heating in air in a temperature range between 250° and 700°C .

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Example 2

A catalyst composition was prepared as described in Example 1, except that the resulting composition was heated at 420°C in flowing nitrogen for two hours to convert the combustible binder precursor into a combustible binder. The side crushing strength (SCS) was 5.8 lbs*mm⁻¹. The carbon content of this catalyst composition was 4.4 wt%. It could be confirmed by TGA that the catalyst composition is stable under hydrogen atmosphere (50 vol% of hydrogen in helium) up to a temperature of 370°C. It could further be confirmed by TGA that the combustible binder can be removed by heating in air in a temperature range between 350° and 700°C.

Comparative Example A

A mixed metal composition was prepared as described in Example 1. The resulting wet filter cake was mixed. During the mixing, the amount of water was adjusted by heating, so that an extrudable mix was obtained. The mixture was then extruded, dried at 120°C, and calcined at 300°C in air. The side crushing strength (SCS) was 4.6 lbs*mm⁻¹. This example shows that the side crushing strength of the resulting catalyst is reduced considerably if a combustible binder is absent.

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Claims

1. A process for preparing a catalyst composition comprising a Group VIII non-noble metal, a Group VIB metal, and a combustible binder, wherein the catalyst comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition, which process comprises contacting a Group VIII non-noble metal component with a Group VIB metal component in the presence of a liquid, wherein a combustible binder material selected from a combustible binder or a precursor thereof is added prior to, during and/or subsequent to the contacting of the metal components, with the proviso that at least if the combustible binder material is a precursor of a combustible binder, this precursor is converted into a combustible binder subsequent to its addition.
2. The process of claim 1 wherein at least one Group VIII non-noble metal component is contacted with at least two Group VIB metal components, resulting in a catalyst composition comprising at least one Group VIII non-noble metal and at least two Group VI metals.
3. The process of claim 1 or 2 wherein contacting of the metal components comprises combining and reacting the metal components in solution to form a precipitate.
4. The process of claim 1 or 2 wherein contacting of the metal components comprises combining and reacting the metal components in the presence of a protic liquid, with at least one of the metal components remaining at least partly in the solid state during the entire process.
5. The process of any one of the preceding claims wherein the Group VIB metal and the Group VIII non-noble metal comprise nickel and/or cobalt, molybdenum, and tungsten.

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6. The process of any one of the preceding claims wherein the combustible binder material is a combustible binder which comprises carbon as its major component.
- 5 7. The process of any one of the preceding claims wherein the combustible binder material is a combustible binder precursor which comprises an organic polymer selected from the group of polyacrylonitriles, bakelite, polyamides, polyurethanes, cellulose and derivatives thereof, hemicellulosic materials, polyfurfuryl alcohol, styrene-divinylbenzene copolymers, phenol resins, furan resins, polyimide resins, polyphenylene resins, phenolic foams, and polyurethane foams.
- 10
8. The process of any one of the preceding claims wherein the precursor of the combustible binder is converted into the combustible binder by pyrolysis in an inert atmosphere at a temperature in the range of 300° - 600°C.
- 15
9. The process of any one of the preceding claims wherein the process comprises the further steps of spray-drying, (flash) drying, milling, kneading, slurry-mixing, dry or wet mixing, shaping, calcining and/or sulphiding.
- 20
10. A catalyst composition obtainable by the process of any one of the preceding claims.
11. A catalyst composition comprising a Group VIII non-noble metal, a Group VIB metal, and a combustible binder, wherein the catalyst comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition.
- 25
12. The catalyst composition of claim 10 or 11 wherein the catalyst composition comprises at least one Group VIII non-noble metal and at least two Group VIB metals.
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13. Use of the catalyst composition of claims 10 - 12 for the hydroprocessing of hydrocarbon feedstocks.
14. A process for the recycling of a used or waste catalyst composition comprising a Group VIII non-noble metal, a Group VIB metal, and a combustible binder, wherein the catalyst comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition, which process comprises thermally treating the used or waste catalyst composition in an oxygen-containing atmosphere at a temperature of at least 300°C.
15. The process of claim 14 wherein the used or waste catalyst comprises at least one Group VIII non-noble metal and at least two Group VIB metals.

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Abstract

The invention pertains to a process for preparing a catalyst composition comprising a Group VIII non-noble metal, a Group VIB metal, and a combustible binder, wherein the catalyst comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition, which process comprises contacting a Group VIII non-noble metal component with a Group VIB metal component in the presence of a liquid, wherein a combustible binder material selected from a combustible binder or a precursor thereof is added prior to, during and/or subsequent to the contacting of the metal components, with the proviso that at least if the combustible binder material consists essentially of a precursor of a combustible binder, this precursor is converted into a combustible binder subsequent to its addition.

The invention further pertains to catalysts comprising a Group VIII non-noble metal, a Group VIB metal, and a combustible binder, wherein the catalyst comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition, and to the use thereof in hydroprocessing. Finally, the invention is directed to the recycling of used or waste catalysts comprising a Group VIII non-noble metal, a Group VIB metal, and a combustible binder, wherein the catalyst comprises at least 1 wt% of carbon as part of the combustible binder, based on the total weight of the catalyst composition.